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Effect of Microwave Heating on The Migration of Additives From PS, PP and PET Container Into Food Simulants

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Effect of Microwave Heating on The Migration of Additives From PS, PP and PET Container Into Food Simulants

by

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M. S. DEGREE THESIS

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Abstract

Microwave food packaging has become a tremendous element in the food manufacturing process. The purpose of any food packaging regulations concerned with the safety of the food is to control and limit the migration of substances from the packaging into the food. The main objective of this thesis is to test three different microwaving packaging materials that are the most common material in the market, viz. polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET), migrated into four food simulant solutions. Four different simulant solutions were used based on the food type and FDA recommendations and regulations. These food simulants include vegetable pure oil, 3% (v/v) aqueous acetic acid, 15% (v/v) ethanol, and olive oil in the temperature of 100°C.

Headspace gas chromatography with mass spectrometric detection (GC/MS) was used to determine the relative migration values from packaging materials into food by putting the materials into contact with simulants for 10 days in temperature of 5°C.

The analyzed results show that the migrations of food package are dependent on microwaving time, package material types and simulant types. The polystyrene (PS) caused the fastest relative migration in olive oil while the polyethylene terephthalate (PET) has the most relative migration in food simulant containing 15% ethanol.

In addition, acetaldehyde, which may be hazardous to consumers, was found in both 3% aqueous acetic acid and olive oil after 10 minutes microwaving from PET.

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Introduction

Microwave Packaging

The number of microwave oven households owned has increased from 1% in 1971 to 25% by 1986 in U.S (Buffler, 1993). Over the last few years, it has become an indispensable part of every household provide convenience and a variety of meal options for home cooking on a daily basis (Ozen & Floros, 2001). Today, more than 90% of U.S. households own a microwave oven.

Microwave ovens generate non-ionizing microwave radiation at a frequency of 2.45 GHz to raise the temperature inside the food with less energy loss. It can cause polarized molecules in the food such as water, fat or other substances to rotate the build up thermal energy, which called a process of dielectric heating. Therefore, it is efficient for the foods with high in water content compared to conventional oven that is more suitable for browning and caramelizing food. Many studies have addressed the nutritional content of food components such as vitamins, minerals and proteins during processing in microwave as equal to or even better than those processed in the conventional oven because of the shorter heating times experienced in microwave heating (Brody & Marsh, 1997).

Packaging materials for microwave heating are classified in different categories depending on how they react to microwaves within the oven. The two common materials are microwave transparent plastics and microwave susceptors (Lentz & Crossett, 1988). Microwave transparent materials, are also referred to as passive packages, do not react to the microwave field (Bohrer and Brown, 2001). In these types of packages, the microwaves penetrate the transparent material and are absorbed by the food. All plastics currently used in food packaging are transparent to microwaves. The most common plastics used in in microwave packaging are polypropylene (PP) or polyethylene terephthalate (PET) due to their high melting point (Belcher, 2006). Another type of microwave packaging materials is known as microwave susceptors. These materials absorb microwave energy and re-emit that energy to the food. Microwave susceptors are utilized in heating, browning and crisping products such as microwaveable fruit pies, popcorn and crust pizza in a microwave oven. They are multilayered, usually made of PET film coated with particulate aluminum and laminated to paperboard.

Microwave packaging market is estimated to reach $2.52 Billion by 2015 in the U.S announced by GIA (Global Industry Analysts) and frozen foods still remain the dominant application for microwave food market, accounting for nearly 60% of total demand in 2012. In addition, the fresh prepared foods market, remains the fastest growing to meet consumer's demand based on their higher quality than frozen foods. The overall goal of this study is to design an appropriate migration study and evaluate migration levels from microwave packaging materials that are polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) into four types of food simulants that are pure vegetable oil, 3% acetic acid, 15% ethanol and olive oil during microwave heating. Two methods from the Food and Drug Administration (FDA) and European Union (EU) regulations are used to evaluate the possible new compounds may be found due to degradation of the additives or polymers during the microwave heating.

Problem Definition

In the USA, the Food and Drug Administration (FDA) regulate packaging materials for food contact. Both the FDA regulations (found in Title 21 of the Code of Federal Regulations, part 170 to 199) and the European Community (EC) (Commission Directives 89/109/EEC) have complex regulations to control potentially harmful migrating substances from food packaging materials. Food safety is a priority for the FDA and EC. However, there are no specific requirements for microwave food-contact containers. There is guidance on plastic containers used in the microwave cooking, in the form of recommendations on chemistry information. Companies need to check compliance of this guidance with considerable amount of migration testing for their products.

Based on these regulations above, however, if the raw materials or production of plastics were not processed properly, some of the chemical compounds such as monomers, additives or catalysts from plastic materials of microwave package may leach out from food containers and cause bad odors, taste even lead to harmful effect to health risk. Some of the packaging material may reduce the amount of energy that should have been absorbed by food by absorbing certain amount of microwave energy. Generally speaking, it has been demonstrated that when food is heated inside plastic package in microwave oven may result in intensified migration of package components. And also migrating new compounds into fatty and liquid with high water content foods will be higher than that into solid, dry foods during microwave heating. Therefore, the aim of this thesis is to review critically the existing procedures about migration modeling first, and then analyze the effect of plastic type in combination with four different types of food simulants to gain more knowledge on unpredictable migration behaviors during high temperature conditions for consumer.

The objectives of this thesis are as followings:

1. To comprehensively and quantitatively investigate the percentage of migration from polymer food packaging during microwave heating at different time span and temperature.

2. To evaluate the possible new compounds may be found due to degradation of the additives or polymers during the microwave heating.

As a framework directive, the aim of regulations for food packaging materials is consumer protection from packaging to foodstuff. In the early of 1980s, the Commission Directive implemented the first Community method of analysis for the official control of vinyl chloride monomer level in food packaging materials. Currently, the limit of overall migration was set at 10 $\mu g/dm^2$ or 60 mg/kg of food stimulant. In the U.S, FDA regulates materials intended to come into contact with a food or beverage, including plastic packaging, as “indirect” food additives. According to FDA, indirect food additives “are substances that may come into contact with food as part of packaging or processing equipment, but are not intended to be added directly to food.” That means it also evaluates adjutants that were added to a polymer in the process of fabricating the final food package. The focus is on United Stated and European Union Requirements.

Literature Review

History and development of microwave food packaging

Growth in the US microwave packaging market has been improved in high-quality package structures for overcoming limitations in terms of browning and crisping even offered some of the flavors include maple brown super, butter and roasted garlic in new product innovations. To use food aroma as a way to improve the microwave experience, a technology is available that incorporates flavor additives directly into plastic packaging. As the package heats in the microwave oven, the aromas are released into the air. The result is substantially increased aroma during cooking, when opening the microwave, and particularly when consumers eat the product from a ready-to-serve package(Ohlsson, 1983). Because approximately 90% of taste is a result of the sense of smell, the taste and flavor of the food are significantly enhanced. Therefore, packaging can be almost as important as food formulation in the overall success of a microwavable product. There is another unique packaging concept called "Intelligent Double Pressure Cooking Technology" for fresh food. In the first cooking phase, when the food is still cold, the microwave energy penetrates deeply into food tissue and converts into heat. The food's water content transforms into steam, which cooks the food from the inside out. In the second phase, as the steam exits the food tissue, it is captured and retained inside the Steam Chef package. As the steam pressure builds, the food cooks from the outside in. More and more smart and simple microwave packaging for refrigerated and frozen foods provide convenience and a variety of meal options.

Frozen foods still remain the dominant application for microwave packaging, accounting for nearly 60% of total demand in 2008, shown in Figure 4. In addition, fresh prepared foods will become available in microwave market through 2013 to meet consumer demand based on their higher quality than frozen and canned alternatives.

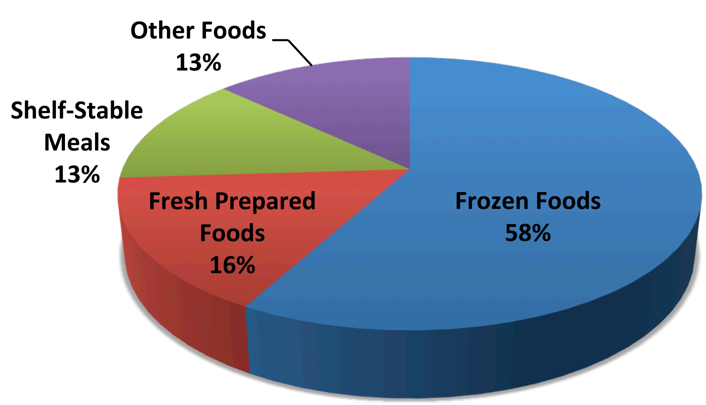


Figure 1 Microwave food market application (2008)

The new generation of microwave products includes meals, snacks, and everything in between, ranging from fresh chicken, precooked entrees, and side dishes to roasted turkey Panini, French fries, Popcorn and pizza. A growing number of microwave products are entering the market in single-serve, portable packages, shown in Figure 5(Kerry, O'grady, & Hogan, 2006).

Figure 2 Common microwave food packaging material

Materials

Polystyrene: $(C_8H_8)_n$

Polystyrene is made by polymerization of monomer styrene. It is derived from petroleum and natural gas by-products through polymerization of styrene monomers. The polymerization reaction of polystyrene is presented in Figure 1.

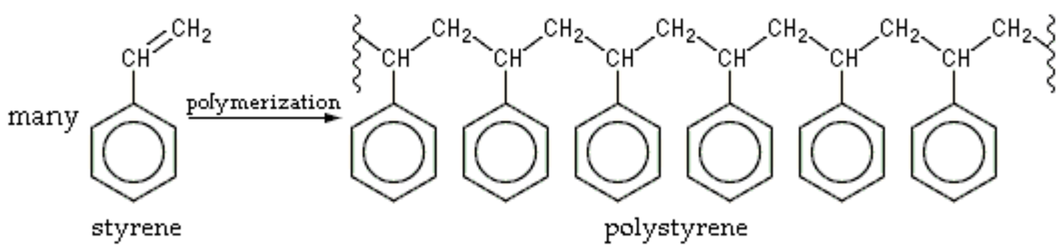


Figure 3 Polymerization reaction of polystyrene(Carolina, 2000)

Polystyrene has a relatively low melting point and poor impact resistance. As an inexpensive and hard, lightweight, low-strength plastic, polystyrene is suitable for protective and insulating packaging industry based on its performance characteristics, quality, and less costly (Piringer & Baner, 2008). To increase the properties of polystyrene, some studies show that adding agents such as butane and pentane during polymerization so that it can be used for poultry, food and beverage containers and other products can form polystyrene. Polystyrene is also can be molded to make very large components for building insulation, automobile, home appliances and toys to help cut energy costs.

Polystyrene plastics packaging which comes into direct contact with foods and beverages complies with the safety requirements in the relevant European Directives on “food contact plastics”. They are produced into the form of trays for meat, fruit and vegetables; container for fast foods, and disposable cups for beverages. The average thickness range that used for food packaging is 0.3 to 6.4 mm.

Some studies indicate that oriented polystyrene or expanded polystyrene for food service are non-toxic, do not migrate into the food to cause contamination under normal uses and are safe for normal everyday use in applications ranging from hot coffee cups and ice cream containers (Lickly, Lehr, & Welsh, 1995). However, in terms of hazard to human health, during polymerization processing, there are concerns that an occupational health risks for styrene workers due to spontaneous abortions and styrene exposure, which may have depressive effects on hepatic dysfunction, leukemia and central nervous system(Tawfik & Huyghebaert, 1998). Some components of products made of polystyrene are might generally find their way into contents during heating or microwaving, causing oestrogenic and potentially adverse health effects in consumers(Sinclair, 1996).

Polypropylene: $(C_3H_6)_n$

In March 1954, Giulio Natta found the first propylene as a crystalline isotactic polymer during Ziegler-Natta polymerization. Later on, syndiotactic polypropylene was also first synthesized by Giulio Natta and his coworkers. The Ziegler-Natta polymerization of propylene is copolymerized with ethylene shown in Figure 2.

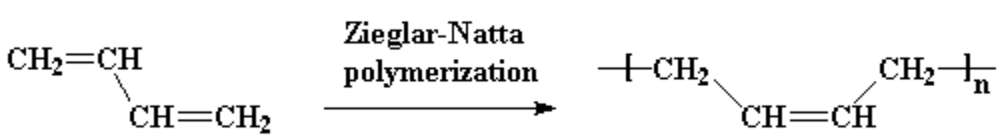


Figure 4 The Ziegler-Natta polymerization(Mississippi, 2005)

There are two common chemical chain structures in polypropylene that are atactic polypropylene and isotactic polypropylene. Isotactic polypropylene become to the most commercial polypropylene during its manufacture. With its own unique characteristics, polypropylene has a wide variety of uses as both as plastic and a fiber(Brewis & Briggs, 1981). As a plastic, it is a clear glossy packaging material with high tensile strength and puncture resistance for food containers and most plastic living hinges without getting melt below 160^oC, or 320^oF(Castle, Mayo, & Gilbert, 1989). As a fiber, compared to nylon, it has moderate permeability to moisture, gases and odors, which are widely used to make indoor-outdoor colored clothing and home furnishings, especially carpeting as it's easily seen around golf filed and home.

In the US market, polypropylene makes up to 2.1% of the plastic bottle market, and is the second largest portion of the most common plastic type used for microwave oven in reusable food containers (Song, Begley, Paquette, & Komolprasert, 2003).

During polymerization processing, there are thousands of possible additives added into polypropylene that could produce some unknown toxic chemicals which can be health risks (Ahmed, 1982). It is necessary to establish a link between the maximum temperature the container in contact with different food stimulants during heating or microwaving and migration of polypropylene additives since some additives are even carcinogens and have concern on endocrine disorder. Therefore, it is important that polypropylene products in the market should be designed to minimize overall migration limitation of additives during food manufacturing operations such as microwave heating.

Polyethylene Terephthalate ($C_{10}H_8O_4$)$_n$

PET is polymerized from ethylene glycol and terephthalic acid as presented in Figure 3.

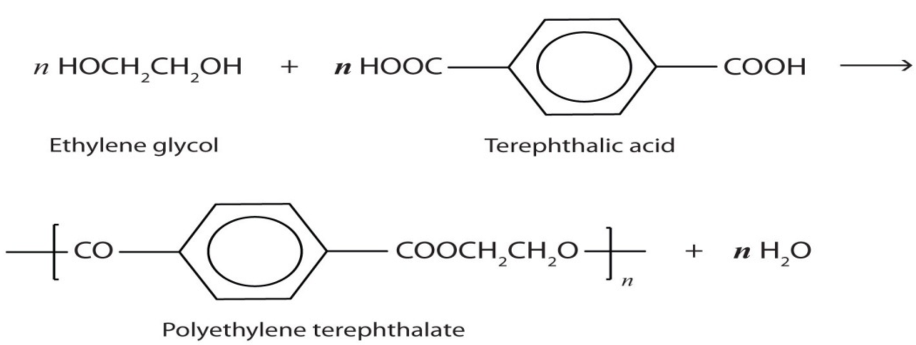


Figure 5 Polymerization reaction of PET(Timberlake, 2002)

As an engineering thermoplastic substance, PET can be fabricated as two separate states – a semi-crystalline polymer like X-ray film in flexible packaging developed in the late 1950s and amorphous fully glass-like transparent such as mineral water in beverage packaging (Kim, Gilbert, & Johnson, 1990). Due to the intrinsic properties of PET polymer, it provides adequate gas barrier properties, particularly against oxygen, carbon dioxide and also exhibits a shatter-resistant property that helps to explain its use in large-capacity containers but weight less than 1.5 Liter (48.oz).

During thermal degradation of the production of PET, there is some acetaldehyde formed when the temperature reaches above the melting point of thermal chemical reactions (Mutsuga et al., 2006). Acetaldehyde (CH_3CHO) is a naturally harmless organic chemical and an approved additive, which can be found in many, fruits, wine and baked goods as a citrus flavor ingredient and a result of lactic acid fermentation. Compared with other plastics, there are not too much additives added in the manufacturing of PET (Widén, Leufvén, & Nielsen, 2004) However, it has been said that there is an amount of toxic substances called diethylhydroxylamine (DEHA) leaching into product. It will pose a risk to human health and cause liver problem. Therefore, consumers should be aware of regulations on the use of PET without reusing them.

PET development as a prime packaging material includes an ongoing process of container performance optimization and light weighting ranging from blisters to soft drink bottles. PET takes up approximately 31% of plastic bottles produced in the United States and the scale is reaching to 200 million pounds per year(Richardson, 2004). PET is fully recyclable with the resin identification code of “1”. The major recycle processes of PET include reclaimed PET (carpet, apparel and non-food contact applications) with many areas in the U.S having implemented curbside and collection service for consumers, incineration for energy recovery which reduced the volume of waste up to 90%, and landfills (Ashby, 1988). In Europe, PET is becoming the most promising candidate for reuse as a food packaging material since its low-diffusivity (Feron, Jetten, De Kruijf, & Van Den Berg, 1994).

Additives in polymeric packaging

Many polymer packaging materials contain a variety of an “additives” to enhance the performances either during processing of manufacturing or in use of polymeric packaging materials that comes in contact with food (ARVANITOYANNIS & Bosnea, 2004). There are more than 1,000 additives including antioxidants, plasticizers, stabilizers, lubricants and antistatic agents. Migration is tested in packaging due to the effects that certain polymer additives have on the human body(Huang et al., 2012).

Acetyl tributyl citrate (ATBC) is the most widely used plasticizer in cling-films made of polyvinylidene. It is innocuous and compatible with PVC, cellulose resin and vinyl chloride copolymers. These types of materials are widely used in microwave oven, especially in home-use applications (García, Silva, Cooper, Franz, & Losada, 2006).

Benzene might migrate into food from contaminated PET bottles. In 1994, a survey was conducted by the UK Food Safety Directorate to measure benzene in plastic food packaging and the migration into food (Franz, Mauer, & Welle, 2004). Dynamic headspace gas chromatography is the widely used technique for the determination of the benzene levels,. It was also demonstrated that benzene and alkyl benzene could be generated from several types of food contact plastics in high temperature applications(Lau & Wong, 2000).

Hydrogen peroxide is commonly used as a sterilization agent for polypropylene and polyethylene aseptic food packaging. It's been shown that a method to evaluate the migration levels as well as the effects of hydrogen peroxide sterilization on the migration characteristics of polypropylene and polyethylene materials.

The impact of migration

In general, food-packaging interactions can be divided into three groups: migration, which is the transfer of packaging components into food; sorption, which is the transfer of food components to the packaging; and permeation, which is the transfer of components through the packaging in either direction(Ahvenainen, 2003). The process of migration of additives from microwave packaging material to food may be separated into three states: diffusion within the polymer, solution at the polymer-food interface, and dispersion into bulk food.

Migration has become a major factor in regulations regarding the safety and quality of packaged food (T. Begley et al., 2005). The degree of migration is determined by various factors including the properties of real food, cooking temperature and power, chemical nature of substances in polymer and food simulants. There are three different microwave container applications, which are microwave susceptor packaging, dual-oven trays and microwavable containers (Ozen & Floros, 2001). Microwave susceptors are usually made of metallized film, ceramics or aluminum flakes. The use of a susceptor for browning and crisping in the microwave oven has been applied to foods such as popcorn, pizza, Panini. Dual-oven trays are usually made of CPET or PP, they are resistant to fatty foods and can be taken from the freezer, placed directly into microwave oven because of the high heat stability.

To get better result of migration, the test should use three aqueous-based food simulants and higher cooking temperature than normal direction on the package since real food is too difficult to analyze (Risch, 2009).

Migration is a diffusion process subject to both kinetic and thermodynamic controls. Therefore, the process is a function of time, temperature, material thickness, amount of migrant in the material, etc. The kinetic dimension of migration dictates how fast the process occurs, i.e., the rate of migration influenced by Polymer properties such as density and crystallinity of polymer, thermodynamic properties that enhanced by different additives produced during the processing of manufacturing, and glass transition temperature (Tg) influence the rate of migration.

Diffusion of chemical substances from polymers is a very complex process, and is dependent on several parameters, such as concentration of substances in packaging film and food, nature of the foods, temperature, and the time period over which duration of contact occurs.

The migration of substances from packaging material into foodstuffs is characterized by diffusion. Diffusion is the mas transfer due to random movement of molecules from regions of higher concentration to regions of lower concentration. However, diffusion rate is a function of only temperature, and is not affected by concentration. In that case, when we put frozen food in to microwave oven, the activity of the macroscopic molecular structures inside of plastic start so become higher and higher, the higher of heating temperature, the higher the flexibility of the polymer molecules and thus the higher the migration rates as described in Figure 6.The glass transition temperature (Tg) of the polymer determines the flexibility of the polymer molecules from a hard, glassy state into a molten or rubbery state. Below Tg, the polymer molecules are brittle (glassy state) and the chance of a migrant finding a sufficiently large hole is limited. Above Tg, the polymer molecules are highly soft and flexible (rubbery state), which makes this chance higher. Therefore, in general, the lower the Tg of a polymer, the higher the migration rates from that polymer. The thermodynamic dimension of migration dictates how extensive the transfer will be. For example, if the migrant has a higher affinity for the food more than for the packaging material, then it will migrate extensively into the food. Hence, thermodynamic properties such as polarity and solubility influence the extent of migration due to interactions between polymer, migrant and food simulant. As an example, for polar polymers such as low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS) with a polar additives, a migrant with poor solubility in food simulants such as 3% acetic acid or water would rather remain in the polymer than migrate into the food simulant. High affinity food stimulant such as pure olive oil or 95% ethanol will increase additive migration and absorption of some certain organic solvents by swelling of the polymer matrix and gaps.

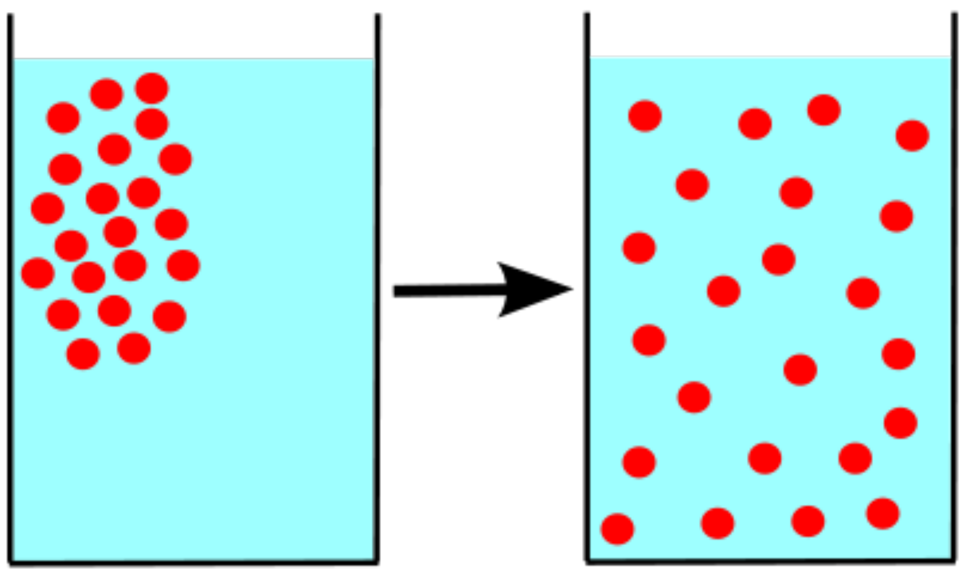


Figure 6 Diffusion in physics

Legislation: Framework Regulation

Because it is quite difficult to draw a strict line to test where the migration of indirect additives into actual foods, making the correct food stimulant for a food packaging migration test is focus on United States (US) and European Union (EU) requirements(Gilbert & Rossi, 2000). To be on the food market, each packaging material should comply with the applicable food contact legislation. In the U.S, FDA defines the regulations. In the EU, it is the Framework Regulation (EC) 1935/2004 for all good contact materials. Under this EU regulation, there are several

Specific and Special Directives, such as the plastic Directive 2002/72/EC and the Vinylchloride Directive 78/142/EC(Commission, 2002). Directive 89/109/EEC is a Framework Directive concerning the general requirements for all plastic materials and articles in contact with food, shown in Figure 7(Commission, 2004). And also Directive 90/128/EEC, subsequent amendment 2001/61/EC deals specifically with the use of plastics in contact with food. Directive 82/711/EEC sets rules for migration testing using specified food simulants. Depending on several factors including the nature of the food to be packaged, the material being tested and the type of food to be in contact with the product. Depending on the type of food when in contact with the product, the Food and Drug Administration's (FDA) defines "Recommendations for Chemistry Data for Indirect Food Additives Petitions", shown in Figure 7.

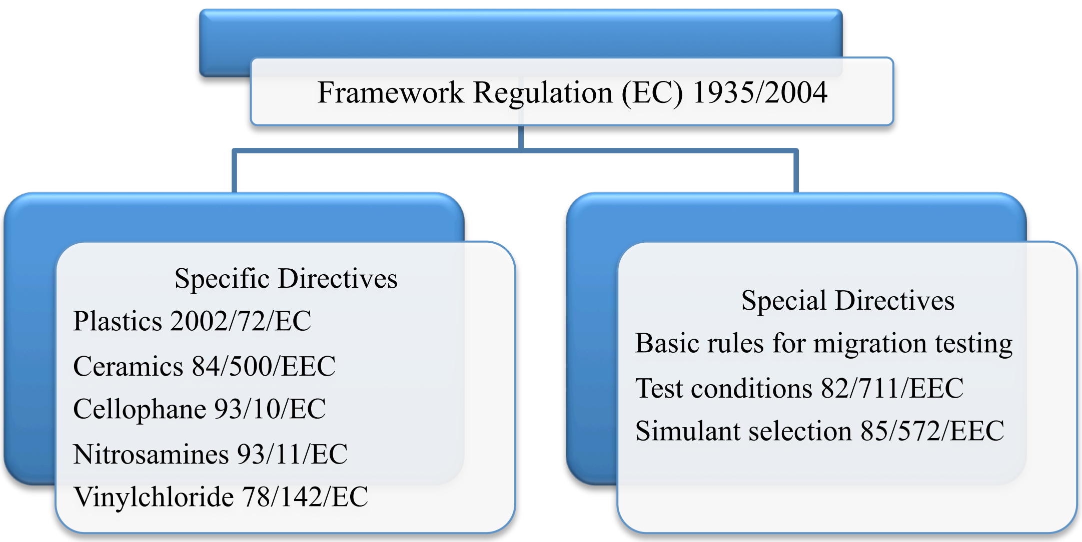


Figure 7 Food contact material legislation in EU

Instrumentation

There are several analytical methods to separate the different components in a mixture prior to analyzing each component and determine migrants in the food contact materials such as microwave susceptors or in foods. The most common techniques used for routine analysis are high performance liquid chromatography coupled with fluorescence detection (HPLC/FLD) or headspace gas chromatography with mass spectrometric detection (GC/MS). Different injectors, columns and interfaces are available to allow for the handling of different types of samples.

Methodology

FDA Recommendations

The FDA recommends stimulants based on the food type. These food types, as defined in the Code of Federal Regulations are shown in Table 1.

Table 1. FDA Classification of Types of Raw and Processed Foods

1. Nonacid, aqueous products; may contain salt or sugar or both (pH above 5.0) (Aqueous)
2. Acid, aqueous products; may contain salt or sugar or both, and including oil-in-water emulsions of low-or high-fat content. (Acidic)
3. Aqueous, acid or nonacid products containing free oil or fat; may contain salt, and including water-in-oil emulsions of low-or high-fat content. (Fatty)
4. Dairy products and modification:
   A. Water-in-oil emulsions, high-or low-fat. (Fatty)
   B. Oil-in-water emulsions, high-or low-fat. (Aqueous)
5. Low-moisture fats and oils. (Fatty)
6. Beverages:
   A. Containing up to 8% alcohol. (Alcoholic)
   B. Nonalcoholic. (Aqueous)
   C. Containing more than 8% alcohol. (Alcoholic)
7. Dry solids with the surface containing no free fat or oil. (None)
8. Dry solids with the surface containing free fat or oil. (Fatty)

Table 1 FDA and EU recommended food simulants

Food Type	Food Simulant	EU Simulant
Aqueous (pH > 4.5)	10% Ethanol	Distilled water
Acidic (pH ≤ 4.5)	10% Ethanol	3% Acetic acid
Alcoholic	10%[a] or 50% Ethanol	10% Ethanol
Fatty	Food oil, HB307[b], or Miglyol 812[c]	Rectified olive oil

[a] 10% ethanol can be used for foods up to 15% alcohol content.

[b] A mixture of synthetic triglycerides, primarily C_{10}, C_{12}, and C_{14}.

[c] A fractionated coconut oil.

Generally, there are three specified food simulant solutions can be used in the experiment based on the federal applicable regulations(Garde, Catala, Gavara, & Hernandez, 2001). These simulants are water, n-heptane, and 8% ethanol. And FDA also allows the use of other several different simulants as alternative food simulant for evaluating migration test are shown in Table 2:

Table 2 Alternative food simulants

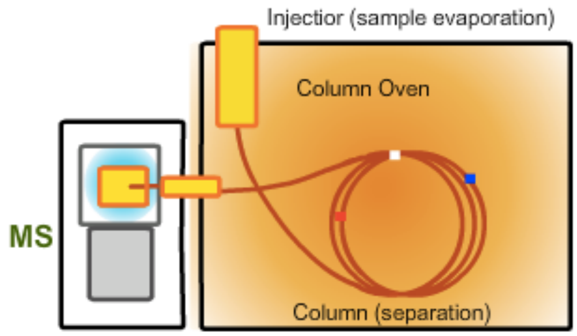
	Simulant Type
Simulant A	Water for aqueous foods
Simulant B	3% w/v acetic acid for acidic foods
Simulant C	15% v/v ethanol for alcoholic products
Simulant D	Rectified olive oil for fatty/oily foods (n-heptane)

Design of Experiment

Instrumentation

The headspace GC/MS technique is very suitable for the volatile compound analysis and it has been used in the EU specific migration(T. H. Begley, Biles, & Hollifield, 1991).

Table 3 Configuration of GC/MS conditions

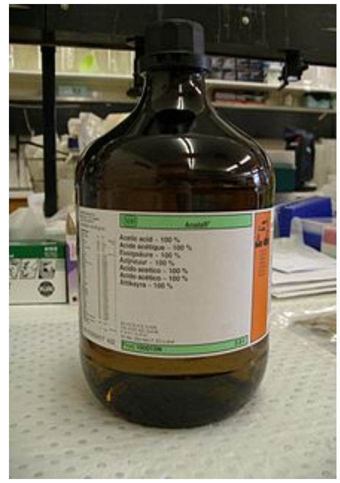


Gas chromatography/ mass spectrometry: Hewlett Packard 5890 Series II	
Column	30m length × 0.25mm ID
Injector temperature	180 ºC
Detector temperature	180 ºC
Carrier gas	Helium
Oven temperature	70 ºC for 5 min; increasing by 10 ºC/min to 120 ºC for 2 min; then by 10 ºC/min to 280 ºC for 5minutes
Split ratio	1:30

Sample selected

Food simulant: Based on FDA recommendations, four different simulant solutions (vegetable oil, 3% aqueous acetic acid, 15% ethanol, and olive oil) were used in the experiment as shown in Figure 8. The vegetable oil and olive oil stands for fatty or oil food with processed meat; 3% w/v acetic acid for acidic foods like fresh vegetable; and 15% v/v ethanol for alcoholic products.

A. Vegetable Oil



B. 3% (v/v) Aqueous Acetic Acid

C. 15% (v/v) Ethanol

D. Olive Oil

Figure 8 Four food simulant solutions

Microwave food-packaging material: Four most common polymer materials purchased from local market to be used for food packaging are sampled and selected for the experiment in Figure 9. In order to accurately assess the samples, clean and empty cup of each product are obtained from their corresponding traders. Mean thickness of PS, PP and PET is 1.7mm, 1.2mm and 0.5mm with non- transparent. Both PS and PP are white with non-transparent and PET is commercial black non-transparent trays, shown in Figure 9.

Material 1 Polypropylene (White)

Thai Mushroom Rice Noodle

Material 2 Polystyrene (White)

Nong Shim Noodle Soup

Material 3 Polyethylene Terephthalate

(Black) Smart Ones Bistro

Material 4 Polyethylene Terephthalate

(Black) Healthy Choice Cuisine

Figure 9 Four most common polymer material in the market

Migration Testing method and analysis:

Firstly, cut 5mm x 5mm of the plastic material and put them into sealed vials of 7 cm^3 by 4 cm^3 of 15ml food simulant solution in Figure 10. The simulation of package-food contact during storage prior to microwaving was carried out under the circumstances of European Commission Directive 93/8/EEC. Store all the samples in the refrigerator for 10 days in temperature of 5°C.

Figure 10 Samples in the experiment.

1. Quantification of sample vials

After 10-day storage in the refrigerator in temperature of 5°C, all the samples were microwaved. Output power of the oven was 540 W, and it was determined according to ASTM F-1317-90 that is the standard test method for calibration of microwave ovens. For each combination of package/solution, 5 microwaving duration spans, ranging from 0 to 10 minutes, were applied. A total of 96 samples were tested for total migration. To avoid overheating of the seals, single exposure took 30s followed with intensive cooling of vials in iced water. Number of these cycles was depending on cumulative exposure time required.

Number of sample materials	4
Number of food simulants	4
Number of microwaving spans	6
Total number of experiments	96

Table 4 List of performed experiment

An extract of food simulant (1-2ml) was transferred to a respective 10 ml of glass vial after 10-day storage, and the vial was closed with a silicone stopper and enclosed with an aluminum crimp. The samples used to develop methods for testing was evaporated under a stream of helium at room temperature to a volume of 20 ml and analyzed by headspace GC-MS.

Headspace silver aluminum crimp caps 20mm | PTFE/white silicone septa 20mm | Headspace crimp top vial 10ml, 23 × 46mm, clear

Figure 11 Preparation of vial

Data and Results

Relative migration

Relative migration addresses that the ratio of actual migration level to the beginning 0 values obtained just after storage =100%. Table 5-8 shows the original data from GC/MS.

Based on the Figure 12-15 of the thesis, the x-axis is the cumulative microwaving time from 0 to 10 minutes with 2-minute step. The y-axis is the relative migration. Here we compared the results based on four different materials, PP, PS, and two types of PET, which are indicated with different color. At the beginning 0 minute, because the microwave is not operated, there is no migration, and the simulant is 100% food simulants. When the microwave begins to be operated with longer time, the migrations from these four different plastics are also increased accordingly, especially after the 4-minute period. It is shown that these four different materials present different behavior, but these curves have similar trend.

As shown in Figure 12 and 13, PP presents most dramatic change compared to the other three materials. However, when the materials are immersed in ethanol and olive oil, the PS and PET present much higher migration compared to the other two materials, and PP presents relatively better behavior in this case. The most dramatic rise of migration is carried out from white polystyrene cup into olive oil (Figure 14), as cumulative exposure time extended 10 minutes. Relative migration values in olive oil reach level of 167% in comparison with initial samples in the previous 8 minutes.

Table 5 GC/MS results in food simulant A (vegetable oil)

Microwaving Time (Minute)	Percent of Material 1	Percent of Material 2	Percent of Material 3	Percent of Material 4
0	100	83.2	88.88	89.01
2	88.9	83.8	84.71	88.05
4	100	82.95	85.1	88.13
6	100	87.11	85,64	88.77
8	89.53	80.7	92.94	96.62
10	77	76.2	82.81	87.42

Table 6 GC/MS results in food simulant B (3 % aqueous acetic acid)

Microwaving Time (Minute)	Percent of Material 1	Percent of Material 2	Percent of Material 3	Percent of Material 4
0	23.51	19.9	14.15	17.54
2	11.39	16.4	13.77	16.45
4	12.49	12.12	11.36	18.07
6	13.95	9.37	11.32	11.63
8	8.41	10.67	9.91	10.24
10	6.98	10.37	3.76	8.43

Table 7 GC/MS results in food simulant C (15% ethanol)

Microwaving Time (Minute)	Percent of Material 1	Percent of Material 2	Percent of Material 3	Percent of Material 4
0	79.82	65.54	81.94	77.66
2	76.47	58.58	81.39	79.01
4	43.33	34.37	34.75	48.59
6	37.19	42.98	20.29	40.78
8	36.67	13.74	29.22	28.43
10	27.67	6.27	10.47	55.46

Table 8 GC/MS results in food simulant D (olive oil)

Microwaving Time (Minute)	Percent of Material 1	Percent of Material 2	Percent of Material 3	Percent of Material 4
0	100.82	100	97.44	72.08
2	100	98.3	100	77.88
4	100.16	100	100	75.02
6	94.64	98.07	100	49.7
8	100.7	98.78	100	11.14
10	109.11	31.51	100	4.85

The curves of relative migration of four different polymer materials as function of cumulative microwaving time are shown in Figures 12-15.

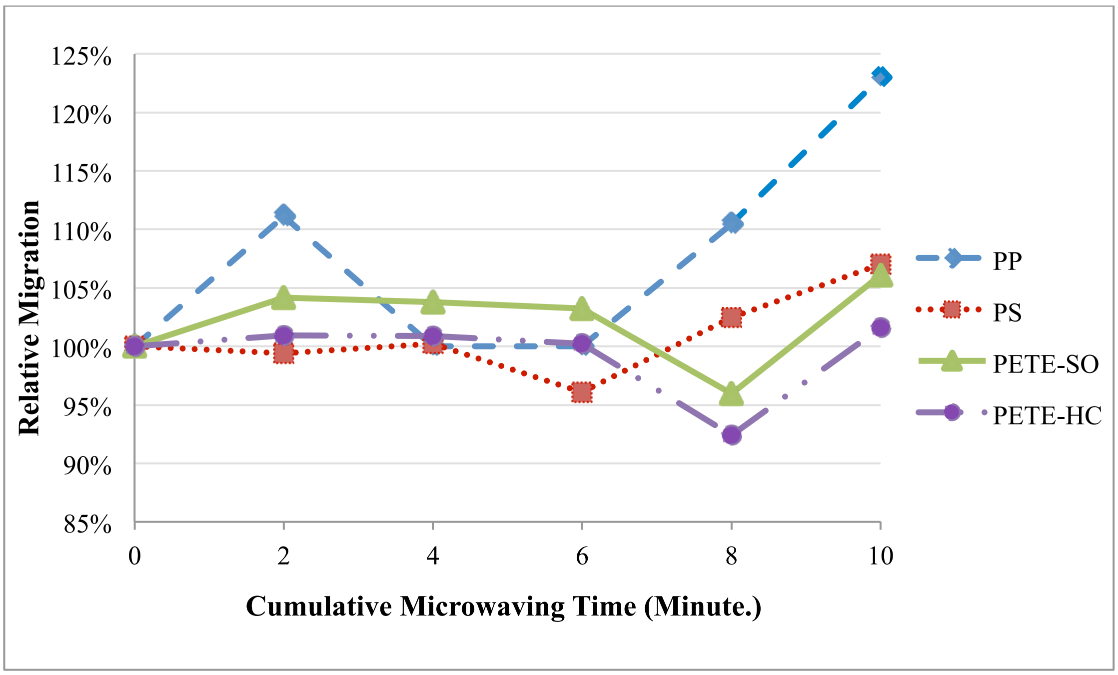


Figure 12 Relative migration values from four containers into food simulant A as a function of microwaving time.

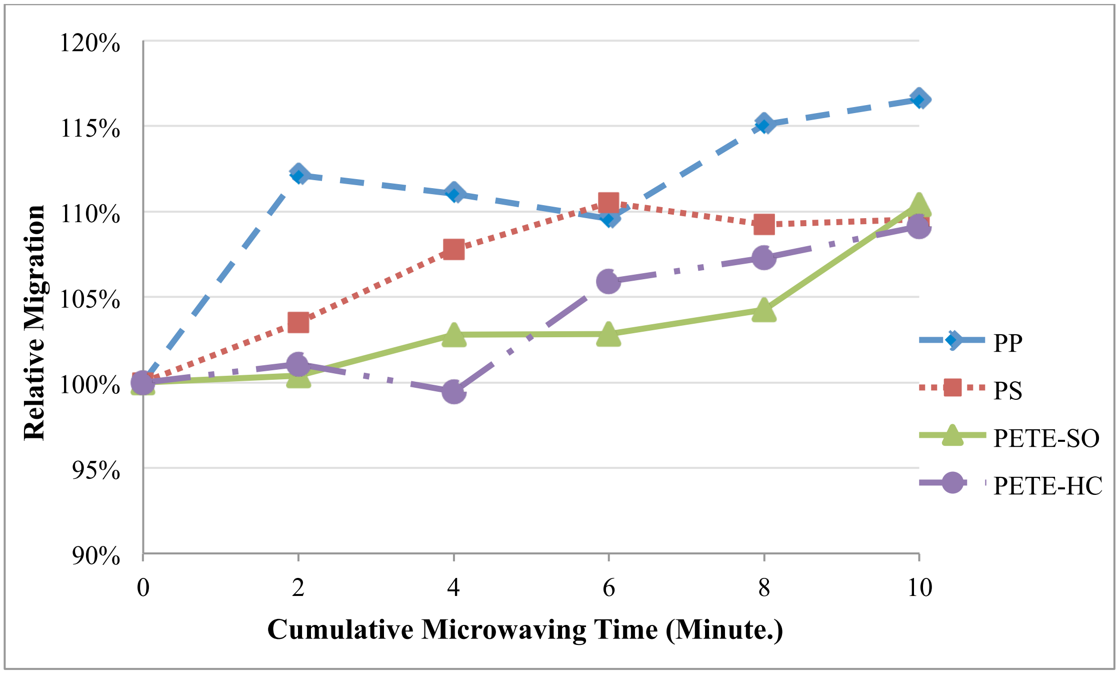


Figure 13 Relative migration values from four containers into food simulant B as a function of microwaving time.

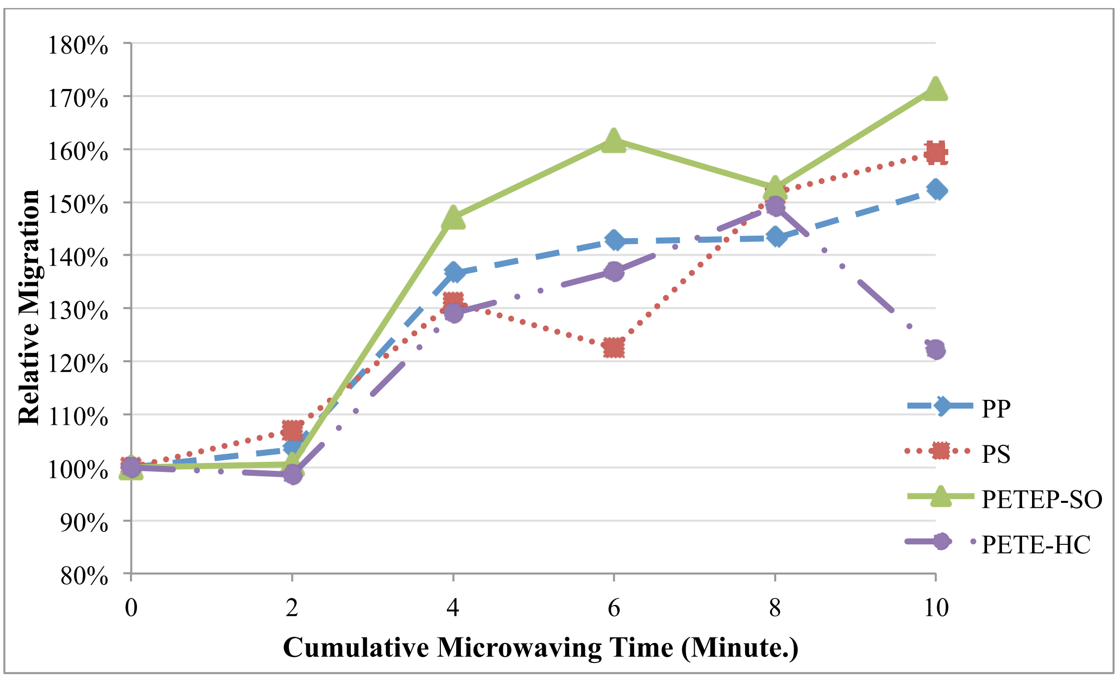


Figure 14 Relative migration values from four containers into food simulant C as a function of microwaving time.

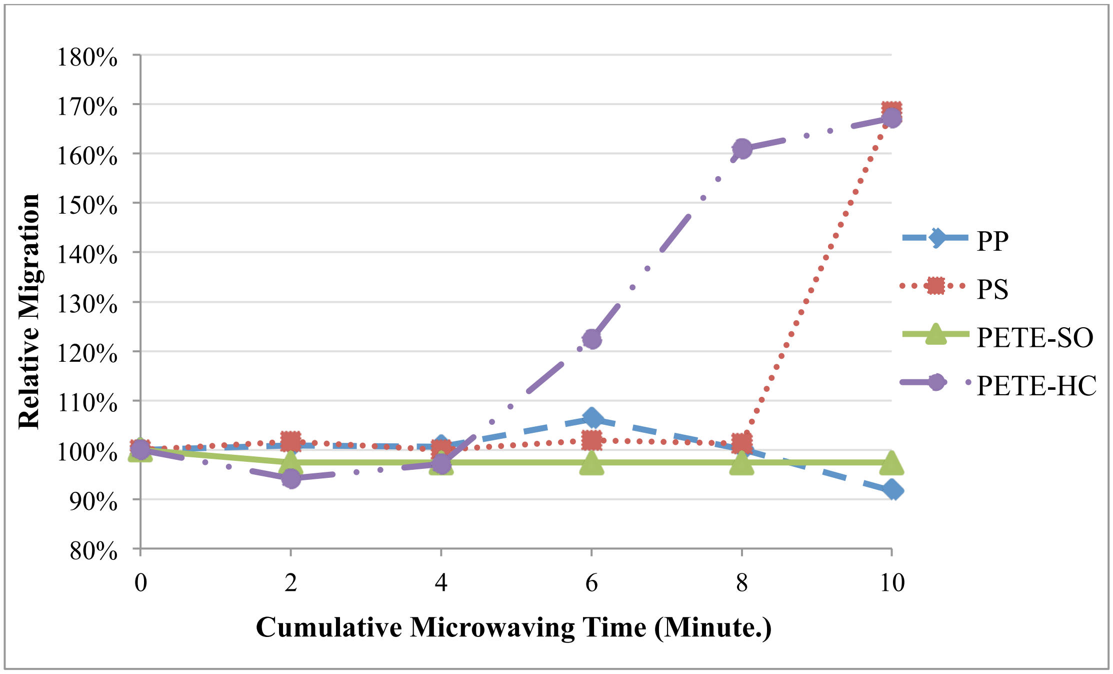


Figure 15 Relative migration values from four containers into food simulant D as a function of microwaving time.

The results are further analyzed by comparing the results when the microwave was operated after 10 min. The migrations of the four different materials in each simulant are averaged, and the results are compared in this Figure. It can be seen that different simulants present different amount of averaged migration. It is shown that the vegetable pure oil and acetic acid generate relative less migration, while 15% ethanol results in the most migration in Figure 16.

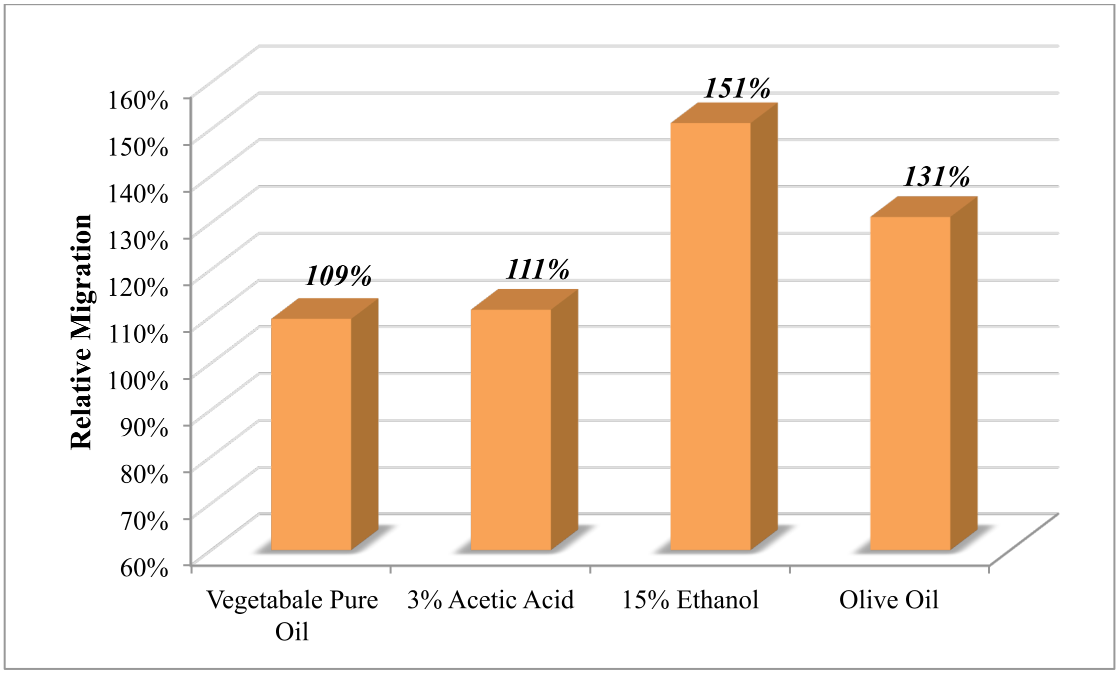


Figure 16 Average of four total relative migration values after microwaving for 10 minutes into four food simulants

Migration of substances

Table 9 Migration of substance result from PET

Microwaving Time (Minute)	**Food Simulant**			
	Vegetable pure oil	3% aqueous acetic acid	15% ethanol	Olive oil
0	N	N	N	N
2	N	Y	N	N
4	N	N	N	N
6	N	N	N	Y
8	N	Y	N	Y
10	N	Y	N	Y

As microwaving time increases, a particular substance acetaldehyde has been found in the GC-MS results on both 3% aqueous acetic acid and olive oil. During the manufacturing of synthetic PET, acetaldehyde is formed as a thermal degradation product when the temperature reaches the melting point (Nijssen, Kamperman, & Jetten, 1996). Acetaldehyde usually occurs naturally in ripe fruits, vegetables and coffee. It can also be used as lactic acid fermentation in chees, flavoring agent in fish preservative, and alcohol fermentation in wine(Ozlem, 2008). The properties of acetaldehyde include high water solubility, distinct fruity and pleasant odor and taste. In that case, even though the PET is suitable for regulations, it is concluded that these PET microwavable containers might be raised to critical levels with increasing temperature for acetaldehyde migration and should not be superheated in microwave especially when the food has lots of acidic or fatty content.

Conclusions

This thesis has shown the effects of microwave heating on polystyrene (PS), polypropylene (PS) and polyethylene terephthalate (PET) food packages immersed in four different food simulants with respect to the migration of chemical compounds from plastic additives.

To analyze and quantitatively detect the migrating compounds, GC-MS has been used to observe migrations into food simulants. The polystyrene (PS) caused the fastest relative migration in olive oil while the polyethylene terephthalate (PET) has the most relative migration in food simulant containing 15% ethanol. By averaging the migrations of the four different materials in each food simulant, it has been shown that the use of ethanol as a fatty food simulant during microwave heating can lead to significant migration

With the increase of microwaving time, in contact with foods simulant, acetaldehyde migration from PET package into food is more substantial. Therefore, PET bottle manufacturers must be very careful in critical control points of the process and also control the acetaldehyde levels at necessary stages.

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